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学位论文

鈴木仁美



主 論 文

ヤコブセン反応に関する研究
及心の一般的性格
とその機構について

On the Jacobsen Reaction. IV.

Character and Reaction Mechanism.

by Hitomi Suzuki

" On the Jacobsen Reaction. IV. ^{*1} Character and Reaction Mechanism "

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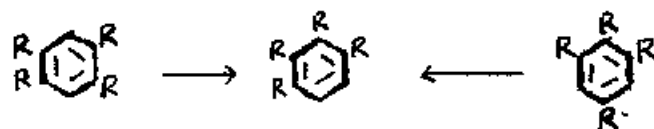
In the electrophilic substitution of higher substituted aromatic compounds, there often observed are the migration or replacement of substituents by attacking groups.¹⁻⁵⁾ Although these phenomena have long been recognized, there are few systematic studies on the scope of such anomalous substitution. The position at which substitution occurs is determined by the group already present in the aromatic ring and usually can be predicted from the rules governing aromatic substitution. As the compounds become more complex, however, it would be difficult to predict the position precisely from the so-called "rules for orientation". This may be because the course of the reaction and the ease with which it takes place, become much more influenced by such factors as the number, structure, types of groups attached to the ring, as well as electronic and steric effects of these groups. Thus the tendency toward orthodox reaction, in which hydrogen is replaced by an attacking group in accordance with the rules of directive influence, is decreased and at the same time

*1. Previous papers in series: (a) R. Goto and H. Suzuki, J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi), 84, 167 (1963). (b) H. Suzuki and R. Goto, *ibid.*, 84, 284 (1963). (c) H. Suzuki and R. Goto, *ibid.*, 84, 425 (1963).

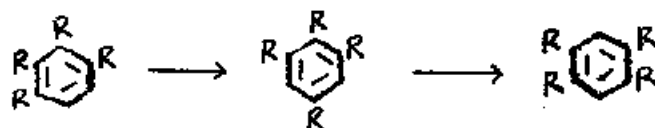
the reaction leading to the production of anomalous products become prominent.

The most typical of these anomalous reaction is the Jacobsen reaction⁶⁻⁹⁾ This name has been given to the migration of an alkyl group or halogen atom of polysubstituted benzene derivatives containing only halogen atoms, only alkyl groups or a combination of the two, which occurs when these substances are sulfonated or their sulfonic acids are allowed to stand in contact with sulfuric acid. One of the most interesting features of this reaction is the migration of an alkyl group or halogen atom to vicinal position. At first sight, this is in direct contrast to the orienting effects in the Friedel-Crafts reaction and long has been the object of much studies.

Jacobsen Reaction

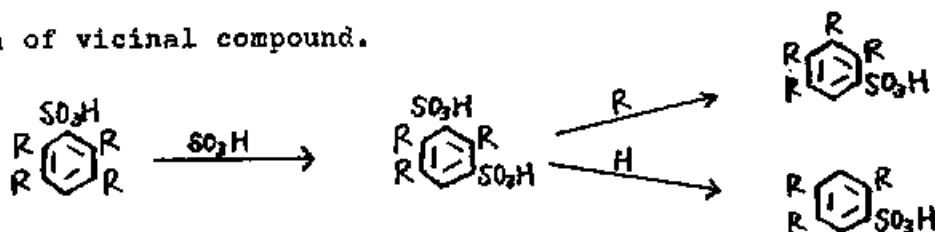


Friedel-Crafts Reaction¹⁰⁾



Although several mechanism have been proposed for this reaction,^{9,11-15)} none of these proposals seems to be satisfactory. Some of them will be cited here:

Arnold and Barnes¹⁴⁾ proposed the following mechanism for the formation of vicinal compound.



According to this theory, the migrating group is detached from the sulfonic acid molecule as a cation by the entrance of a second sulfonic acid group; this cation then replaces the more hindered sulfonic acid group of the di-sulfonic acid. This mechanism is, however, not tenable in view of: (a) the failure to isolate the postulated intermediary di-sulfonic acid; (b) the fact that the migration of an alkyl group occurs, even under the mild conditions under which the formation of di-sulfonic acid is improbable; (c) the failure to explain many reactions involving the migration of halogen atoms; (d) the fact that the conversion of sulfonic acid group into amide or ester exerts an inhibitory effect on the reaction.

Dewar has assumed the intramolecular migration of sulfonic acid group: applied to durene, the reaction can be written as follows;¹⁵⁾



While a plausible explanation for some reaction of simple compounds, this mechanism fails when attempts are made to apply it to a variety of compounds which undergo the reaction. For example, since sulfonic acid group always takes the less blocked position, sulfonation of 5-substituted pseudocumene occurs preferentially at β -position. Thus one would expect, according to his theory, 4-substituted hemimellitene as a sole product from 5-substituted pseudocumene. This is, however,

not the case as 5-ethylpseudo-cumene affords chiefly 5-ethylpseudo-cumene, whereas 5-isopropylpseudo-cumene gives no vicinal compound. Moreover, this mechanism is inconsistent with the fact that durene itself undergoes the Jacobsen reaction more readily than isodurene. His mechanism also cannot be applied to the halogen migration.

Fieser and Fieser¹⁶⁾ have explained the reaction on the basis of allylic type rearrangement of substituent group:



The above mechanism, in which the sulfonic acid is first protonated to form the arenium ion, which undergoes allylic migration of a sulfonic acid group and reverse migration of a methyl group, followed by expulsion of a proton to form prehnitene sulfonic acid, is untenable since it cannot be used satisfactorily to explain either the formation of vicinal compounds from unsym-tetraalkyl or pentaalkyl-benzenes, or most of the reaction involving the migration of a halogen atom.

Thus no mechanism has been found which will explain satisfactorily all the available data. This probably might be because several mechanisms are responsible for the Jacobsen reaction. Much of the studies on the mechanism of the reaction so far have been concerned with the reactions involved in the formation of vicinal compounds. In addition to these somewhat peculiar reaction, however, there exist a number of reactions which should be classed as the Jacobsen

reaction in the sense that they involve the migration of an alkyl group or halogen atom in the course of sulfonation. Therefore it is apparent that a single mechanism capable of accounting for all the variations of the Jacobsen reaction cannot be postulated on the basis of such simple assumption mentioned above.

In this paper, the author would like first to summarize all the results of his studies, together with some of previous workers, hitherto being made on the Jacobsen reactions and then, classifying them according to their reaction types into three groups, to propose more reasonable mechanism consistent with all the data.

Experimental Procedure

Details of the experimental procedure and results were given in the previous papers in series I - III, and will not be repeated here.

A. The Jacobsen Reactions.

1. Polyalkylbenzenes. The general procedure was as follows: a mixture of the hydrocarbon and sulfonic acid was magnetically stirred and gradually heated on a water bath. The color changed from yellow to red, then depending to reddish brown, and finally black. Complete solution of the hydrocarbon was usually effected at 60 - 80°C. The mixture was kept at this temperature range for 4 - 6 hrs. and then allowed to stand for a day or two at room temperature. The mixture was diluted somewhat with water and any solid

was removed by filtration. The filtrate was distilled with superheated steam, the distillate was extracted with ether, the extract was washed with aqueous sodium hydroxide and dried over calcium chloride. Then the solvent was evaporated and the residual oily material was fractionated.

II. Polyalkylhalogenobenzenes and Polyhalobenzenes.

A standard procedure for conducting the experiments with these compounds was divided into two, depending upon the solubilities of the reaction products. In procedure I, the whole reaction mixture was poured onto ice and any solid was removed by filtration. The solid was washed, dried and subjected to the chromatographic separation on alumina column. To the sulfuric acid filtrate was added saturated sodium chloride solution to precipitate the sodium sulfonate. The salt was filtered and converted to sulfonamide, which was then fractionally crystallized. Procedure II was the same as I except for the method of handling the filtrate. The sulfonic acid solution was hydrolysed by passing superheated steam through the filtrate and the distillate was subjected to the fractional distillation.

B. Identification of the Reaction Products.

I. Polyalkylbenzenes. All specimen obtained from the Jacobson reactions were inspected by gas-chromatography and infra-red spectroscopy, and then identified by the conversion to known polybromo or polynitro compounds. The structure proof that all the groups attached

to the ring were located vicinally, was effected either by the oxidation of a portion of specimen with diluted nitric acid to benzene 1,2,3,4-tetracarboxylic acid; or by the transformation of a specimen into a phenanthrophenazine derivative through a dinitro and diamino compound, which proved that the two vacant positions were ortho to each other, that is, all four alkyl substituents were in vicinal position.

II. Polyalkylhalogenobenzenes and Polyhalogenobenzenes.

The oils obtained from hydrolysis of sulfonic acids were carefully fractionated, and each fraction was subjected to the gaschromatographic and infra-red spectroscopic inspection. Vicinal location of all substituent groups was established by the conversion of a specimen to a phenanthrophenazine derivative by the same method as that used in I. Solid crystalline materials were, after chromatographic separation on alumina column, recrystallized from ethanol or benzene, and identified by mixed melting with authentic specimens prepared by the other methods.

Results and Discussion

All the Jacobsen reaction may be divided into two general types, intramolecular and intermolecular; in both cases there are the transfers of alkyl group and halogen atom.

Polyalkylbenzenes. The compounds which yield "abnormal products" are limited almost exclusively to tetra or pentamethylbenzenes containing tetraethylene rings and/or alkyl groups of short,

straight chain, such as methyl, ethyl and n-propyl, while those having alkyl groups of branched structure, such as iso-propyl and t-butyl, elimination of these or other alkyl groups are the only reactions taking place. Mono, di and trialkylbenzenes merely yield sulfonic acids which are quite stable toward sulfuric acid.*2.

The Jacobsen reaction embodies an electrophilic attack upon the ring of polysubstituted benzene and is dependent upon increased electron density at the position of sulfonation. It is readily apparent that an electron-attracting group, such as the nitro or carboxyl group, would inhibit the reaction. The conversion of sulfonic acid group to sulfonamide or ester exerts an inhibitory influence on the migration of an alkyl group. Reagents also exert a definite effect over the course of the reaction: fuming sulfuric acid usually favors sulfonation, whereas common sulfuric acid often brings about migration of alkyl groups. These, and other known facts, suggest that the reversibility of sulfonation is the factor of great importance in determining whether a Jacobsen reaction will take place or not.

The process of the Jacobsen reaction of polyalkylbenzenes may be divided into two stages, and both stages must be met before any Jacobsen reaction can be expected to occur in the sulfonation of polyalkylbenzenes.

(a) The elimination of an alkyl group, which occurs during the sulfonation of polyalkylbenzene relatively resistant to sulfonation owing to its highly crowded structure. In most cases the combined

the combined effects of steric hindrance and the entrance of powerful electron-attracting group are necessary to bring about the expulsion of the migrating group.

(b) The alkyl cation thus ejected migrates, according to its stability, intramolecularly (vicinal orientation) or intermolecularly (disproportionation). The formation of vicinal compound occurs when the migrating alkyl group can readily take the vacant position meta to the entering acid group.

Thus with polyalkylbenzenes containing iso-propyl or t-butyl group, the first stage (a) readily takes place to give bulky cation, which is, however, incapable to participate in the next stage (b) of the reaction.*3. On the other hand, mono, di and trialkylbenzenes are simply sulfonated to give a stable sulfonic acid, from which any alkyl group cannot be removed at all, therefore, with these compounds no reaction analogous Jacobsen proceeds. sym-Hydrindacene has the structure formally similar to those present in octahydroanthracene and Jurene, but it doesn't undergo the reaction on

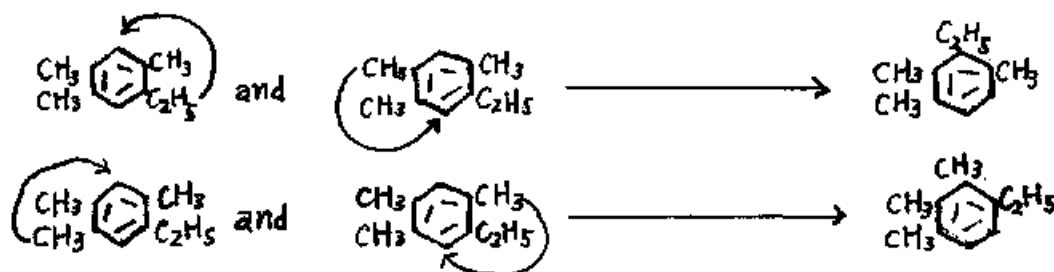
*2. With some di and trialkylbenzenes containing bulky groups, such as isopropyl or t-butyl, elimination of one of these are observed.

*3. Recently, an interesting reaction involving the intramolecular migration of t-butyl group has been reported:

M. Genard, D. Awang, F. L. Chu, Canadian J. Chem. 41, 1756 (1963).

standing with sulfuric acid. It possibly may be explained by the small hindering effects of five-membered rings.

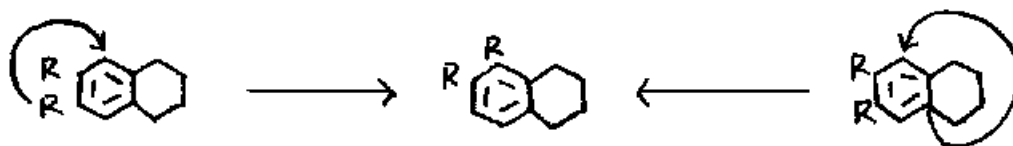
In the Jacobsen reaction of tetraalkylbenzenes, there always formed were small amounts of trialkylbenzenes and hexaalkylbenzenes. Trialkylbenzene fractions obtained from mixed tetraalkylbenzene were mixtures of several compounds. This fact indicates that there is a possibility of the formation of two or more vicinal isomers, depending on which alkyl group may shift toward the vacant position meta to the sulfonic acid group. For example, 5-ethylseudocumene afforded two vicinal isomers, together with considerable amounts of prehnitene.^{*4.}



An experiment conducted upon a mixture of durere and *s,m*-tetraethylbenzene led to a complex mixtures of polyalkylbenzenes in which the chief products were also prehnitene and vic-tetraethylbenzene. This fact indicates that the migration of an alkyl group to vicinal position proceeds intramolecularly. There is apparently the inverse correlation between the ease of a compound to undergo the Jacobsen reaction and the ease with which the compound can be sulfonated. Thus when durere and isodurere were subjected to the action of sulfuric acid under the same conditions, it was noted that the time required for the

complete migration of methyl group was much less with durene than isodurene.

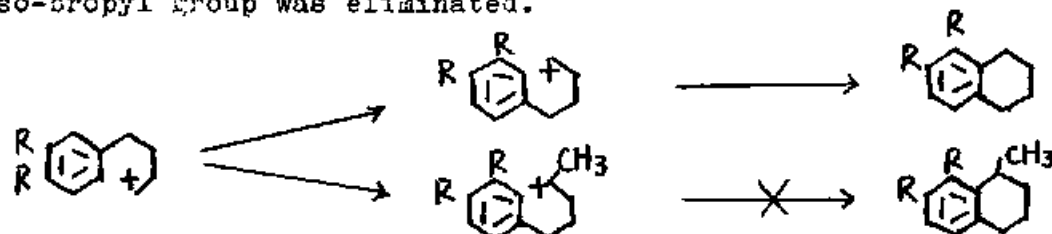
The conversion of 6,7-dialkyltetralins to vicinal compounds can theoretically proceed by two different routes: the alkyl group may migrate from the 6 (or 7) position to the 8 (or 5); and the tetramethylene ring may open and then close in the ortho position to the alkyl group.



The evidence that the main reaction takes place through the latter course may be briefly summarized as follows: (a) the reaction products contained only small amounts of mono-alkyltetralins; (b) octahydroanthracene, in comparison to sym-estradiylbenzene, was much more readily converted to the vicinal compound under the same conditions; (c) when 5,7- and 6,7-dimethyltetralin were subjected to the same conditions of the Jacobsen reaction, the former gave only small amount of oily product which could not be identified, whereas the latter readily converted into the vicinal compound.

*4. The isolation of both these isomers was unsuccessful. Although all possible isomeric products were undoubtedly formed in the reaction of mixed polyalkylbenzene, their presence had been demonstrated or inferred only by a combination of gaschromatography and infra-red spectroscopy, because of the experimental difficulties involved in separation.

Although the opening of a ring followed by the migration of an intermediate having a cationic terminal carbon atom could involve a simultaneous isomerization of the group to the more stable secondary carbonium ion, no hydriodene derivative was detected in the reaction products from di-alkyltetralins. This may be explained both by the well-known preference for the formation of six-membered rather than five-membered ring in cyclization, and by the tendency for bulky cation to avoid a highly blocked position. Di-alkyltetralins containing iso-propyl group were always converted into the compounds in which iso-propyl group was eliminated.

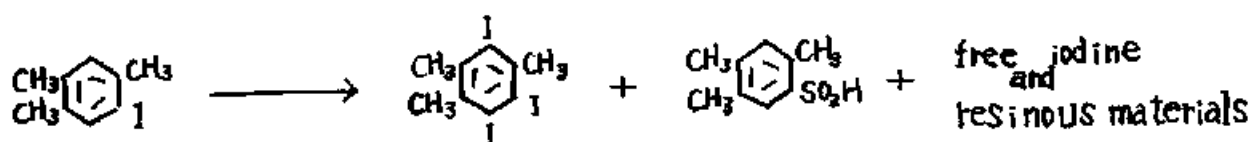
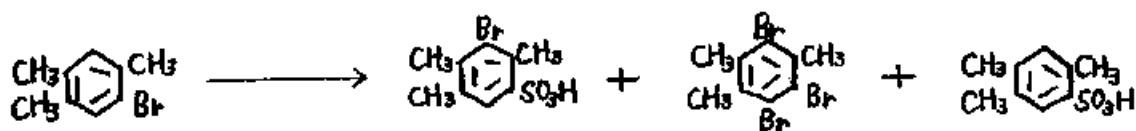
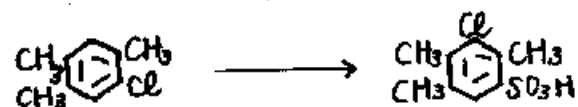


Relatively high yields of vic-di-alkyltetralins compared to those of vicinal tetraalkylbenzenes are attributed to the fact that one end of the long chain cation is attached to the ring and cannot leave the molecule freely. Therefore tetra-n-butylbenzene, with which analogous process might be expected to occur, has not been studied yet, but any formation of vicinal compound can hardly be expected.

Reaction products from mixed polyalkylbenzenes are usually complex mixtures and require extensive purification. Furthermore, the yields are low and the probable structure inferred from analogy should be investigated by independent methods. Thus the Jacobsen reaction cannot be considered as the general synthetic method of vic-tetraalkylbenzenes.







Polyalkylhalogenobenzenes and Polyhalogenobenzenes. An extensive study of the reaction of polyalkylhalogenobenzenes has shown, as would be predicted on the theoretical grounds, that the increasing the number of the alkyl groups attached to the benzene ring favors both migration of halogen atom and decomposition of compound to tarry materials. Thus there exist a certain limited scope within which the reaction can proceed smoothly. For example, monochloroxylenes are merely sulfonated, while monoiodoxylenes afford polyiodoxylenes in high yields; with monochlorotetramethylbenzenes are observed even migration of methyl group, whereas with monoiodotetramethylbenzenes, the reaction goes too readily, yielding intractable resinous materials.

Iodine atom is most readily and chlorine atom least easily replaced by sulfonic acid group; therefore the disproportionation is most prevalent with iodine compounds whereas the formation of vicinal compounds is found with chlorine compounds. Bromine compounds occupies an intermediate place with respect to ease of replacement, hence they show both disproportionation and intramolecular migration simultaneously. The three reactions which follow illustrate this statement well;



iodine cation is unable to re-enter the molecule owing to its bulkiness, and is consequently set free as elementary iodine.

The behavior of a number of sym-polyhalogenobenzenes and poly-alkylhalogenobenzenes toward sulfuric acid is summarized in the following table.

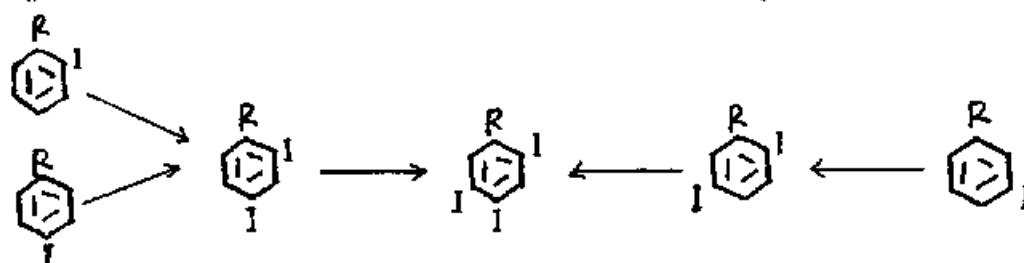
X						
Cl			(+)	+	(+)	+
Br	-	-	+	+ -	(+)	+ -
I	-	-	-	-	-	-

where sign + denotes the formation of vicinal compound; sign - , disproportionation. Parentheses mean that the reaction occurs only under drastic conditions.

With polyhalogenobenzenes the Jacobsen reaction is confined almost entirely to polybromo and polyiodobenzenes. A few special cases involving chlorine migration have been found, but for the most part chlorine atom doesn't undergo the migration. It appears that the halogen atom always migrates intermolecularly if any reaction occurs at all, and all the available evidence indicate that the ease of migration in these compounds is in the order of I > Br > Cl. As is ring-bonded fluorine atom unable to form a cation, it of course cannot take part in migration.

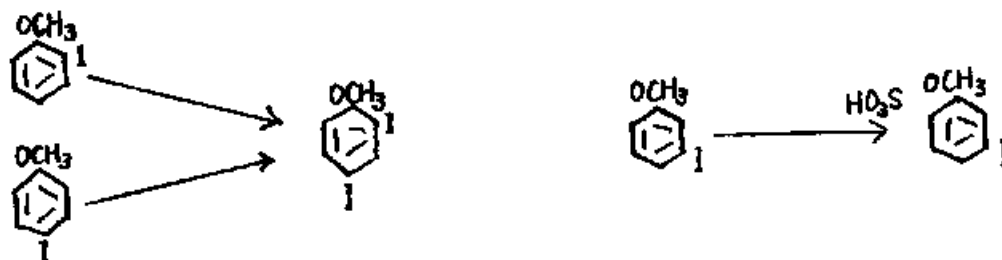
In order to determine the effect of various substituents upon the ease, course and limits of the reaction, the action of sulfuric acid upon a number of halogenobenzene derivatives was studied.

Electron-attracting group, such as the nitro, carboxyl and carbonyl, hindered the reaction so greatly that it usually failed to take place when any of these are attached to the ring. On the other hand, accumulation of electron-releasing groups, such as hydroxy and alkoxy, facilitated the reaction so much that it was often difficult to prevent the compounds from decomposing to tarry materials. The presence of bulky groups, such as iso-propyl and t-butyl, on the aromatic ring also interfered with the reaction. The importance of steric factor was revealed by the examination of products from monoiodoalkylbenzenes; with methyl and ethyl group, the migration products were obtained in high yields, whereas with isopropyl and t-butyl group, the reaction was that leading to the formation of resinous materials, giving no definite product.

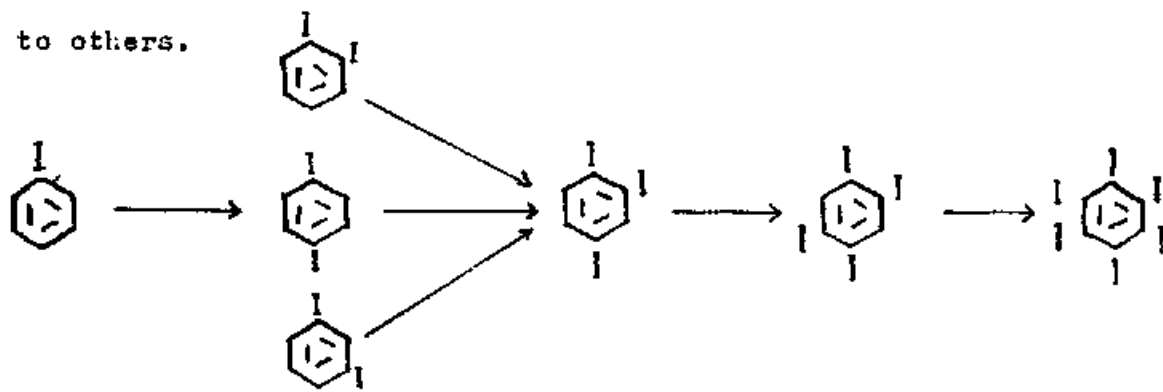


No attack of halogen atom upon the alkyl group was observed.

In some cases, slight changes in the structure of compound may cause great differences in the ease of the migration of halogen atom. For example, o- and p-iodoanisole readily gives polyiodo compounds, but m-isomer is simply sulfonated to give a stable m-sulfonic acid.



The reaction usually proceeds as progressive halogenation of a parent compound, and a certain isomer is always formed in preference to others.



When there exist more than one halogen atoms capable of migration, the preferential replacement occurs with those present at the positions that have higher electron density or greater steric hindrance.



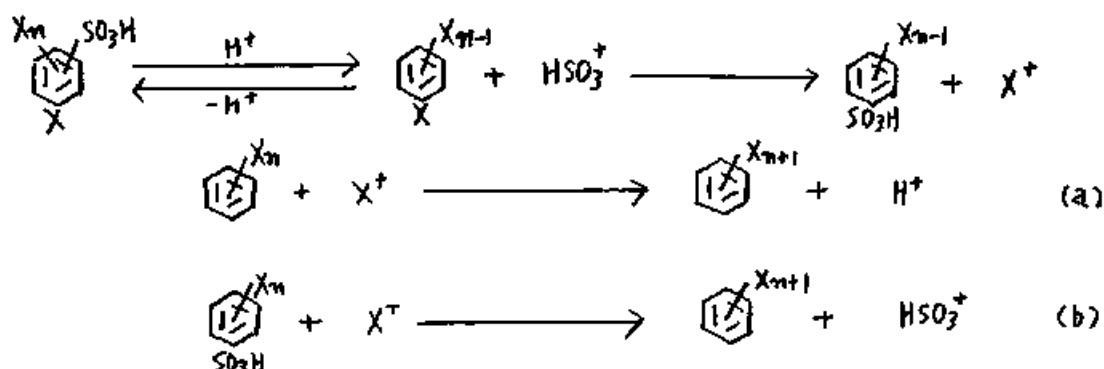
The reaction is considered of such value for the direct synthesis of some polyiodo compounds.¹⁷⁾

Mechanism. All the Jacobson reactions so far observed can be divided into three groups according to their reaction types: the first, shown by a compound relatively resistant to sulfonation owing to its crowded structure, involves an anomalous sulfonation leading to the elimination of an alkyl group or halogen atom, followed by the migration of these; the second, in which normal sulfonation of a compound constitutes the initial phase of the reaction, is most encountered with these compounds which are readily sulfonated to form a stable sulfonic acid. The migration of substituent groups on the ring gradually occurs intra-

or intermolecularly, depending on their structure and experimental conditions; the third, shown by some polycyclic compounds, is concerned with the reactions in which any sulfonation cannot be expected at all because of their highly crowded structures and reduced reactivities. The protonation of the compound followed by the expulsion of iodine cation must constitute the initial phase of the reaction.

In the following discussion, for each individual group of the reactions the author have attempted to formulate a mechanism and with which to explain satisfactorily the experimental results so far obtained on the Jacobsen reaction.

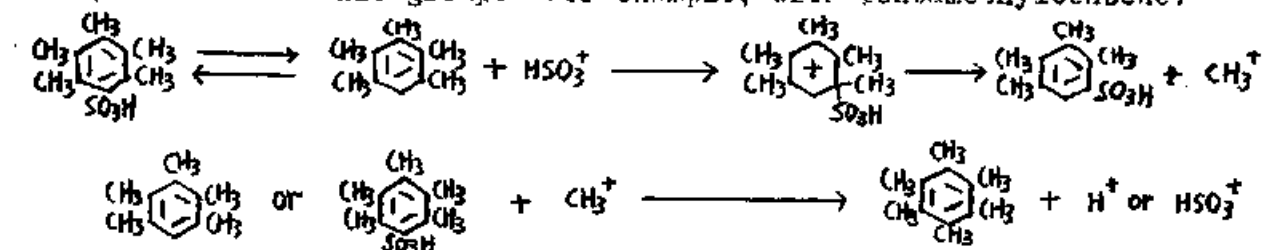
(I) The first group of these are encountered with the compounds relatively difficult to be sulfonated and may be represented by the following generalized scheme.



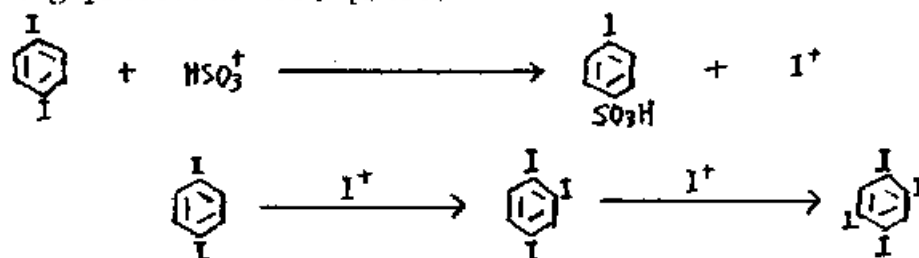
This is a two-stage reaction initiated by the electrophilic attack of a sulfonic acid group, which will, of course, seek a position of high electron density and of small steric hindrance. The alkyl group or halogen cation which is eliminated during sulfonation will react with the parent compound according to the equation (a), or with the sulfonic acid according to the equation (b). The most typical reaction of this

propyl and 5-iodopseudocumene.

Reactions of di-alkyltetralin and pentaalkylbenzene also may be incorporated into this group. For example, with pentamethylbenzene:



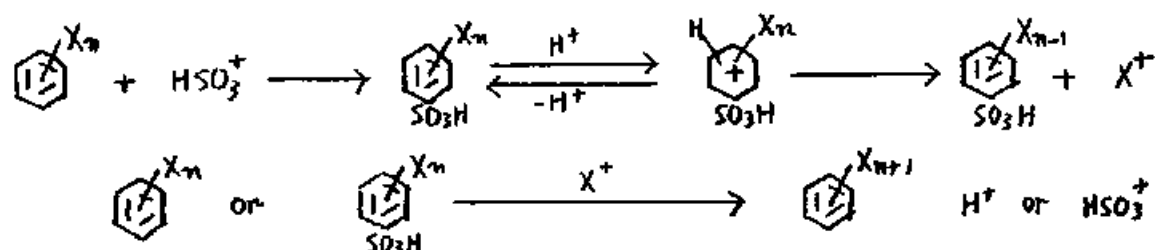
Next, let's consider the compounds having only a few substituent groups. It has long been known that the sulfonation of p-iodobenzene is always accompanied by the disproportionation, thus giving p-iodobenzene sulfonic acid and mixtures of polyiodobenzenes. This process is also represented by the analogous two-stage mechanism, in which the following processes take place.



When some polyalkylbenzenes containing t-butyl groups are allowed to stand in contact with sulfuric acid, the elimination of t-butyl group is observed to some extent. In these cases, however, the extreme aversion of t-butyl group to the entry in a position ortho to alkyl groups in the ring inhibits further alkylation of the parent hydrocarbon, thus no reaction analogous to the Jacobsen proceeds.

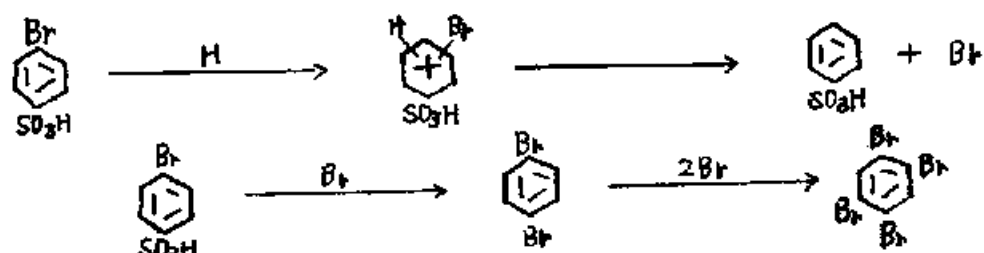
(II) The second group includes the reactions which are most encountered with the compounds readily subject to the action of sulfuric acid. As has been mentioned above, the case of sulfonation is inversely related with that of migration, hence the compounds of this group need more time

for the completion of the reaction. It is best represented by the following generalized scheme.



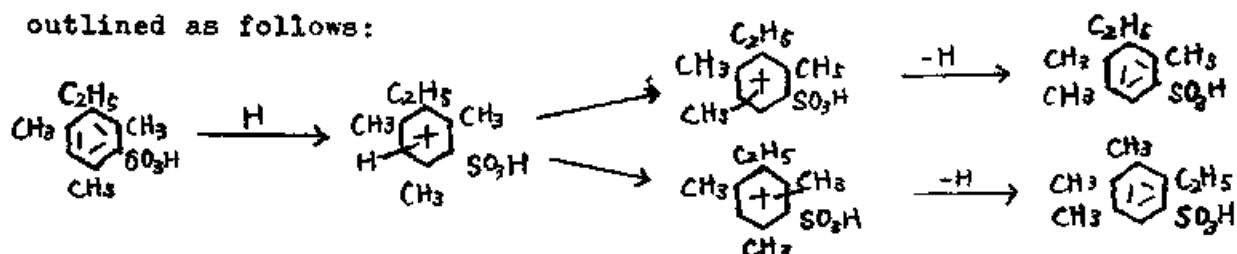
The reaction scheme above is interpreted as follows: sulfonic acid is first protonated to form an intermediate complex, from which ejected is the group present at the position of higher electron density and larger steric hindrance. The alkyl group or halogen atom thus expelled may migrate, according to its stability, intramolecularly to form vicinal compounds, or intermolecularly to yield disproportionation products.

The formation of polybromobenzenes from monobromobenzene is one example.



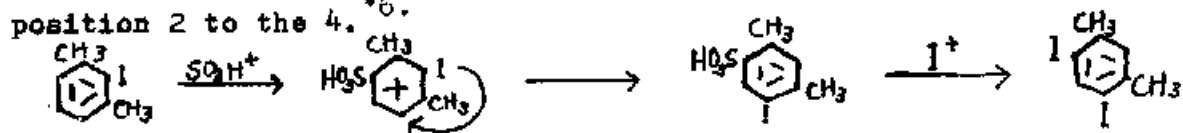
There are two possible routes by which a vicinal compound could be formed from a non-vicinal compound: one is those just described in the group (I), another belongs to this group (II). For example, unsym-tetraalkylbenzenes are necessarily sulfonated ortho to both alkyl groups unless one of them is displaced by the entering sulfonic acid group. Thus there arises great steric hindrance which forces the migration of one of alkyl groups so as to reduce the blocking action

on the sulfonic acid group. Applied to ethylstyrene, this may be outlined as follows:



The vicinal orientation found with unsym-tetraalkylbenzene sulfonic acid is attributed to the buttressing effect of the alkyl group meta to the sulfonic acid group, because *sym*-trialkylbenzene in which no buttressing effect of meta alkyl group is present may never show the Jacobsen reaction.

Another interesting example was found in the reaction of 2-iodo-*m*-xylene and 2,3-diiodotoluene (future communication), where formed was not expected 2,4-diiodo-*m*-xylene nor 2,3,6-triiodotoluene, but the symmetrically substituted 4,6-diiodo-*m*-xylene and 2,4,5-triiodotoluene. These must be formed as a result of initial sulfonation at 6-position followed by the intramolecular shift of iodine atom from the hindered position 2 to the 4.*6.

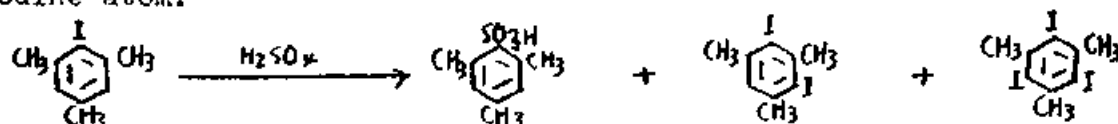


These results further support the concept that the entry of a bulky group in meta position has great influence on the stability of the

*6. As *m*-xylene sulfonic acid and iodine afford no iodinated compound under the same conditions, the intermolecular migration of iodine atom is less probable.

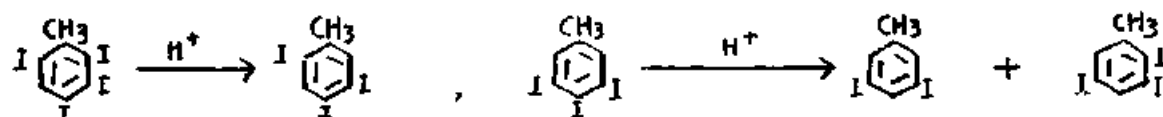
substituent group sterically hindered by two ortho constituents.

Sulfonation of iodomesitylene might be another example, where no reaction proceeds without accompanying the disorientation of iodine atom.¹⁷⁾

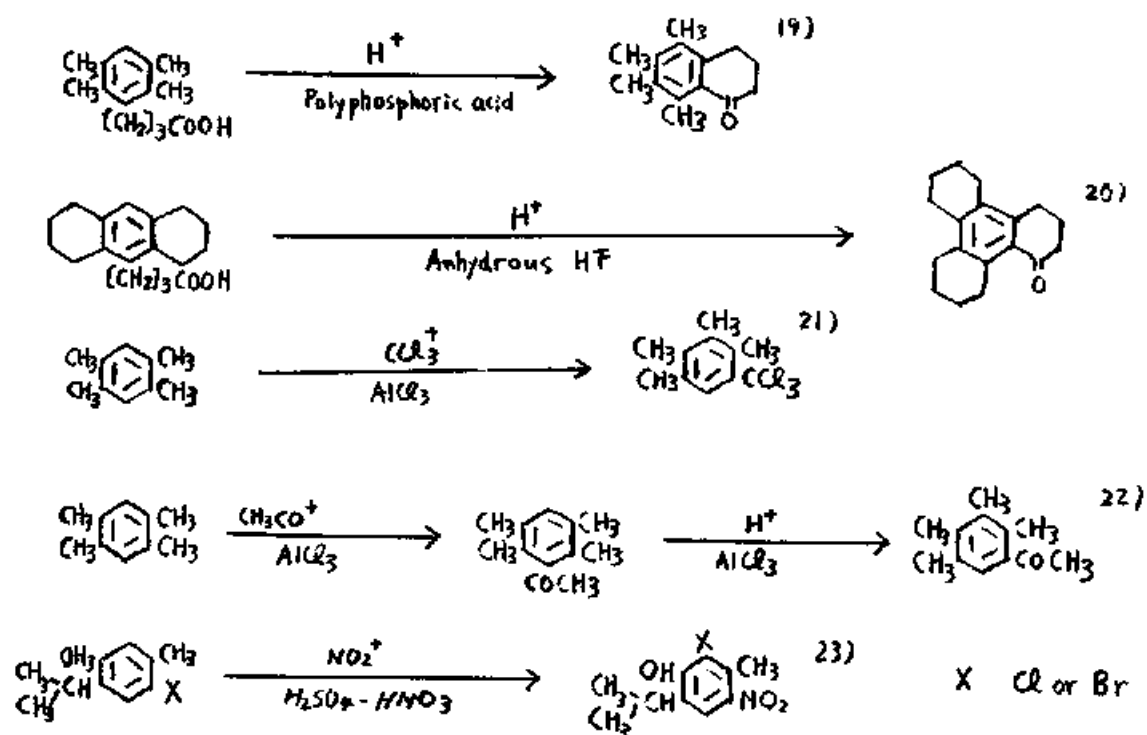


Two types of reaction routes, (I) and (II), however, must be regarded as limiting extremes, and a number of the reactions possibly may take place through a course which could be regarded as a combination of the two. Which type of the reaction predominates depend on the steric requirements of the compound subjected to the Jacobsen reaction. With highly crowded compounds, the reaction scheme (I) involving the direct displacement seems important, whereas, with less crowded compounds the reaction scheme (II) predominates.

(III) The third group is quite different from the two mentioned above, and sulfuric acid appears to act as a protic solvent. Some polyiodo compounds of highly crowded structure, with which any sulfonation can hardly be expected to occur, undergo this type of reaction under the drastic conditions. For example,



This could not be classed as the true Jacobsen reaction, because no sulfonation is involved in the reaction. There are, however, many interesting observations in the literature on the migration of an alkyl group or halogen atom, analogous to the Jacobsen reaction, where, neither sulfonation nor sulfonic acid group is concerned. The following are some examples:



In all cases there are the intra- and/or intermolecular migration, in presence of acidic medium, of an alkyl group or halogen atom involving the vicinal orientation of these groups. If we consider the nitro, carbonyl, or acetyl group plays the same role as that of sulfonic acid group in the Jacobsen reaction, then one might suppose that the above reactions are these of Jacobsen types and may indeed take place by analogous processes.

For classification purpose of these anomalous reactions, it seems convenient to give the term "Jacobsen Reaction" much wider meaning, that is, to extend the definition to the general cases of anomalous electrophilic substitution, in which observed is an intra- or intermolecular

migration of substituent groups expelled by the entry of electrophilic attacking groups under the very influence of acidic solvents. Then the term "Jacobsen Reaction" no longer means only abnormal sulfonation in a narrow sense, but means a variety of anomalous electrophilic substitutions of similar nature which are at present not systematized and included into other categories.

The author wishes to express his gratitude to Professor Ryozo Goto of Kyoto University for his continuous encouragement and helpful discussion throughout this work.

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Literature

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